*The Synthesis of Deuterated Polypropylenes**

By Shunsuke MURAHASHI, Shun'ichi NOZAKURA and Katsutoshi YASUFUKU

(Received January 18, 1964)

The deuteration of polymers is a useful method for the structural study of high polymers. In previous papers,[1] the authors reported the infrared spectroscopic study of deuterated polystyrenes and were led to the conclusion that some of infrared crystalline sensitive bands observed in isotactic polystyrene originate from the helical structure of the polymer.

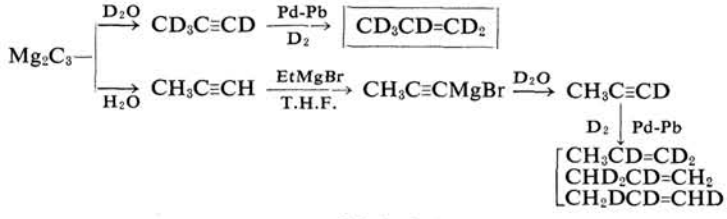
The structure of isotactic polypropylene is being investigated extensively by many authors using infrared spectra of deuterated polymers. Propylene-*cis*-1-d_1, -*trans*-1-d_1,[2] -1, 1-d_2, -2-d_1,[3,4] -3, 3, 3-d_3,[4] and -3-d_1,[5] have hitherto been prepared, and the infrared spectra of their polymers have been discussed.

In the present paper, for the purpose of an infrared spectroscopic study of isotactic polypropylene, the authors carried out the preparation and polymerization of propylene-1, 1, 2-d_3 and -d_6. A recent note by Liang and Lytton[6] on polypropylene-d_6 prompted the present authors to report on the syntheses of the two polymers and on interesting information obtained from the copolymerization of the monomers. A more detailed study of infrared spectra of the polymers will be published elsewhere.

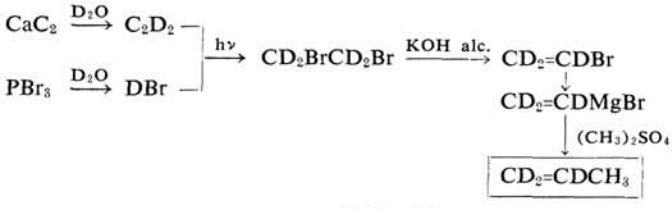
Results and Discussion

Propylene-d_6 was prepared by the half-reduction of deuterated propyne, which had been obtained from the hydrolysis of magnesium carbide (method 1) with deuterium oxide. Method 1 was proved unsuitable for the preparation of propylene-1, 1, 2-d_3. It was, however, successfully prepared by the reaction of deuterated vinyl magnesium bromide (method 2). Methods 3 and 4 were also tried. However, method 3 gave a very low overall yield in preliminary runs, while method 4 gave an impure propyl alcohol which was found rather difficult to purify and so was felt unsuitable for the synthesis of the pure end product.

Propylene-d_6.—Magnesium carbide is the only carbide which gives C_3-acetylenic hydrocarbon on hydrolysis.[7] The preparation of propyne-d_4 from magnesium carbide was reported by Leitch.[8] Using the method of Novak,[7] magnesium carbide was prepared by the reaction of



Method 1



Method 2

* Paper XI in a series on "Stereoregular Polymers." For the preceding paper, see This Bulletin, **35**, 1686 (1962).

1) H. Tadokoro, T. Kitazawa, S. Nozakura and S. Murahashi, *Chem. High Polymer (Kobunshi Kagaku)*, **17**, 231 (1961); This Bulletin, **34**, 381 (1961).

2) G. Natta, *SPE Journal*, **15**, 373 (1959).

3) M. Peraldo and M. Farina, *Chim. e ind.*, **42**, 1349 (1960).

4) C. Y. Liang and M. R. Lytton, *J. Polymer Sci.*, **44**, 549 (1960); **54**, 523 (1961).

5) H. Tadokoro, T. Kitazawa, S. Nozakura and S. Murahashi, This Bulletin, **34**, 1209 (1961).

6) C. Y. Liang and M. R. Lytton, *J. Polymer Sci.*, **61**, S45 (1962).

7) J. Novak, *Z. physik. Chem.*, **73**, 513 (1910).

8) L. C. Leitch and R. Renaud, *Can. J. Chem.*, **30**, 79 (1952).

$$CD_3CDO \xrightarrow[HCl]{EtOH} CD_3CDClOEt \xrightarrow{Br_2} CD_2BrCDBr\text{-}O\text{-}Et$$

$$CD_2BrCDBr\text{-}O\text{-}Et \xrightarrow{CH_3MgBr} CD_2BrC(CH_3)D\text{-}O\text{-}Et$$

$$CD_2BrC(CH_3)D\text{-}O\text{-}Et \xrightarrow{Zn} CD_2{=}CDCH_3$$

Method 3

$$CD_2\text{-}CD_2 \xrightarrow{CH_3MgBr} CH_3CD_2CD_2OH \rightarrow CH_3CD{=}CD_2$$

Method 4

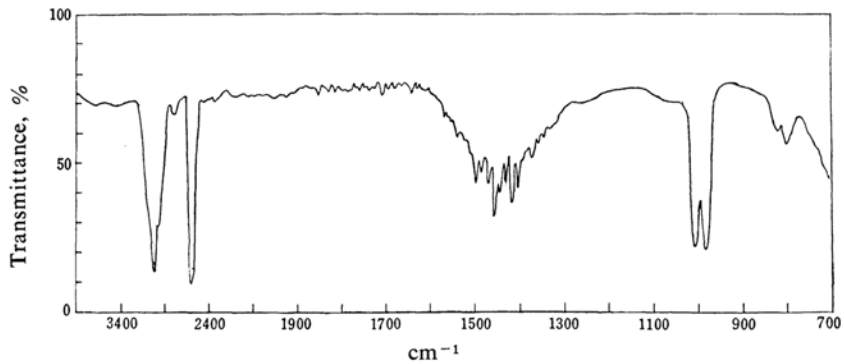


Fig. 1. IR spectrum of propyne-1-d_1.

magnesium metal and *n*-pentane at 680±20°C. Hydrolysis of the carbide with deuterium oxide gave crude propyne-d_4, which contained allene (11.2%) and acetylene (0.4%) as by-products. Acetylene was removed from the crude product by repeated distillation. The propyne, which still contained allene, was used in subsequent hydrogenation without further purification. The degree of the deuteration of propyne was estimated by mass spectrographic analysis to be 88.5%. The product was then deuterated over a Lindlar catalyst to propylene-d_6, which was found to contain a considerable amount of propane-d_8 (15.7%) and the unreacted propyne-d_4 (6.0%) the latter being removed as mercuric salt. The propylene, which still contained propane, was used for the polymerization without further purification, since the existence of propane does not impair the succeeding polymerization or the resulting polymer. The degree of the deuteration of propane-d_8 was found to be 78.7% by mass spectrography, and so that of propylene-d_6 could be estimated to be around 82%.

Method 1 was found to be unsuitable for the synthesis of propylene-1, 1, 2-d_3. Propyne-1-d_1, which was obtained by the hydrolysis of propynyl magnesium bromide with deuterium oxide, was found to be highly deuterated, showing no ≡C–H stretching band at 3300 cm^{-1} and a strong ≡C–D stretching absorption at 2550 cm^{-1} in the infrared spectrum (Fig. 1). After the half-reduction with deuterium, however, the product showed a weak absorption at 3060 cm^{-1}, indicating the presence of $=CH_2$ and/or =CHD. Furthermore, a polymer obtained from this product showed a $-CH_2-$ stretching absorption at 2836 cm^{-1}, the inten-

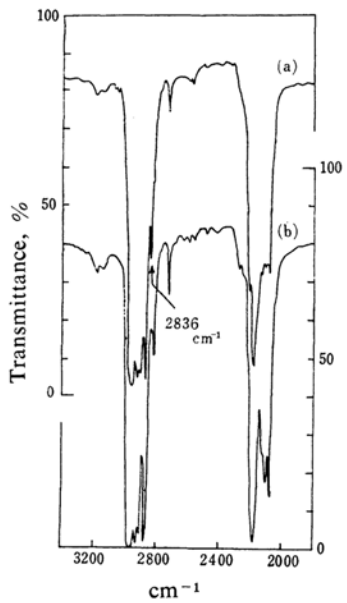


Fig. 2. IR spectra of isotactic polypropylene-1, 1, 2-d_3, (a) prepared by method 1 and (b) by method 2.

sity of which suggests the existence of more than 15% $-CH_2-$ units in total methylene units (Fig. 2). This unexpectedly high $=CH_2$ group content suggests that there is an equilibrium between propyne and allene on the surface of the Lindlar catalyst. The equilibrium concentration of allene at 100°C is known to be about 14%,[9] and allene is known to be more rapidly hydrogenated than propyne.[10] The observed values of more than 15% $-CH_2-$ in the polymer mentioned above indicates the existence of more than 30% allene in the mixture with propyne. Therefore, allene should have been supplied continuously by the isomerization of propyne during hydrogenation.

Propylene-1, 1, 2-d_3.—Propylene-1, 1, 2-d_3 was successfully prepared by method 2 starting from calcium carbide. The yield of the dedeuterobromination product of deutero-dibromoethane was found to be rather low (30%) compared with the yield of more than 70% in the case of the dehydrobromination of dibromoethane. The yield in the former case could not be improved by various modifications of reaction conditions. This may be explained as follows: The reaction can be considered competitive between an elimination and a substitution reaction. It is known that the substitution reaction is usually accelerated by the deuteration of the substrate ($k_D/k_H=\sim1.1$),[11] while the elimination reaction is retarded ($k_D/k_H=1/4\sim1/6$).[12] The observed isotope effect in the yield of vinyl bromide, therefore, may be the result of the composite effect of two competing reactions.

The reaction of deuterated vinyl magnesium bromide with dimethyl sulfate gave propylene-1, 1, 2-d_3 in a good yield. The impurity was found by gas chromatography to consist of very small amounts of ethane and butadiene. Since butadiene was expected to be objectionable in the preparation of the pure polymer, it was removed by repeated distillation. The degree of the deuteration of the propylene-1, 1, 2-d_3 thus prepared was estimated to be fairly high from the fact that its infrared absorption spectrum did not show any of the characteristic absorptions which are ascribed to the other partially-deuterated propylenes[13] (Fig. 3). A notable difference of between the infrared spectrum and those of the other deuteropropylenes is found in the position of the stretching mode of the C=C double bond. Propylene-1, 1, 2-d_3 shows the absorption at 1604 cm^{-1}, while propylene, propylene-2-d_1, -1, 1-d_2, and -d_6 show it at 1651, 1613, 1612 and 1587 cm^{-1} respectively.[14]

Polymerization.—The deuterated propylenes obtained above were polymerized to isotactic polymers with a Ziegler-Natta catalyst. The results are shown in Table I, while infrared spectra of the polymers are presented in Fig. 4.

The Infrared Characteristics of Copolymer.—An interesting fact was observed in the infrared spectrum of the copolymer of propylene-

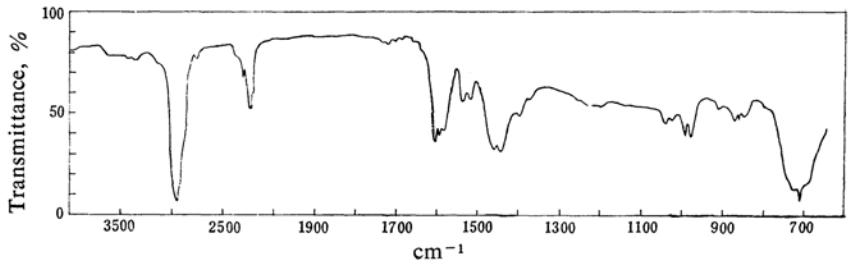


Fig. 3. IR spectrum of propylene-1, 1, 2-d_3.

TABLE I. POLYMERIZATION OF PROPYLENES WITH $TiCl_3$-$AlEt_3$ CATALYST IN HEPTANE AT 60°C

Monomer	g.	Catalyst		Polymn. time hr.	Polymer yield g.	Heptane insoluble part	
		Ti/monomer	Ti/Al			% in total polymer*	M. p. °C
$CD_3CD=CD_2$	ca. 2.3	0.04	1.0	67	1.7	80.9	166
$CH_3CD=CD_2$	ca. 1.3	0.02	0.9	46	1.2	56.0	167

* Extracted with boiling heptane for 10 hr.

9) J. F. Cordes and H. Gunzler, *Chem. Ber.*, **92**, 1055 (1959).
10) G. C. Bond and J. Sheridan, *Trans. Faraday Soc.*, **48**, 651 (1952).
11) S. I. Miller, *J. Phys. Chem.*, **66**, 978 (1962).
12) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).
13) M. Farina and M. Peraldo, *Gazz. chim. ital.*, **90**, 973 (1960).
14) G. Zerbi, M. Peraldo and E. Mantica, International Symposium on Molecular Structure and Spectroscopy, Tokyo, Papers of Abstract, C213-1, 1962.

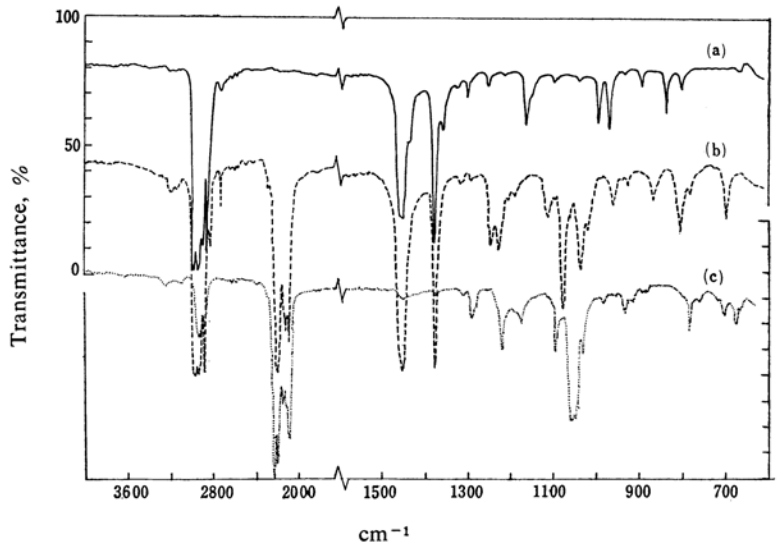


Fig. 4. IR spectra of isotactic polypropylene (a), propylene-1,1,2-d_3 (b), and polypropylene-d_6 (c).

1,1,2-d_3 and propylene. The isotactic copolymer is compared with an artificial mixture of the isotactic homopolymers of these two monomers in Fig. 5. An X-ray examination of the copolymer specimen showed the same order of crystallinity as those of the homopolymers. However, the infrared spectrum of the copolymer is quite dfferent from that of the artificial mixture. The crystalline sensitive bands (shown by arrows in Fig. 5) of polypropylene exist in the spectrum of the artificial mixture, but they do not exist or diminish in that of the copolymer. This suggests that the occurrence of crystalline-sensitive bands in isotactic polypropylene is not due to intermolecular interaction but to intramolecular interaction, as in the case of isotactic polystyrene.[1] If the crystalline-sensitive bands were originated from intermolecular interaction, they would disappear, or at least diminish, in the case of the artificial mixture too. The fact also suggests a random distribution of the deuterated monomer units along a polymer chain, resulting in the complete disturbance of the original intrachain interaction.

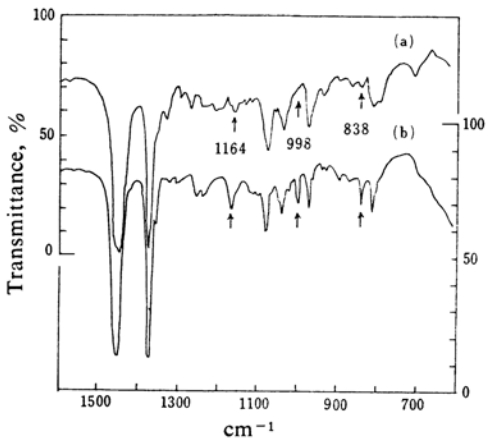


Fig. 5. IR spectra of isotactic propylene-propylene-1,1,2-d_3 copolymer (a), and an artificial mixture of the two homopolymers having the same composition (b). Arrows show the crystalline sensitive bands of the isotactic polypropylene.

Experimental

Mg_2C_3.—Magnesium carbide was prepared by the method of Novak.[7] The vapor of pentane (100 cc.) with a stream of hydrogen was brought into contact with magnesium powder (20 g.) at 680±20°C for 6 hr., yielding 27 g. of the dark gray carbide covered with black carbon powder. On hydrolysis the carbide (20 g.) evolved a gas which was condensed by a dry ice-acetone trap to 14 ml. (−78°C) of liquid products. The gas was found by gas chromatography (1m. silica gel column, 100°C) to be composed of 89.2% propyne, 10.4% allene and 0.4% acetylene.

Propyne-1, 3, 3, 3, d_4.—In a 100 ml. three-necked flask equipped with a stirrer, a condenser and a dropping funnel, magnesium carbide (20 g.) was placed suspended in 50 ml. of dry dioxane. The top of the condenser was connected to a trap kept at about −20°C and then to a collecting trap cooled in dry ice-acetone. Deuterium oxide (26 g., 99.65% purity) was added drop by drop to magnesium carbide at room temperature, yielding 12 ml. (−78°C) of a liquid product. The product was found by gas chromatography to contain 88.4% deuterated propyne, 11.2% deuterated allene and 0.4% deuterated acetylene. In order to remove acetylene, the product was evaporated at about −25°C and condensed at −78°C. Evaporation and

condensation was repeated several times until no acetylene was detected by gas chromatography. The degree of deuteration of the C_3D_4 mixture was found to be 88.5% by mass spectrography.

Propyne-1-d_1.—A mixture of propyne and allene was obtained by the hydrolysis of magnesium carbide with water, and it was freed from acetylene in a manner similar to that mentioned above. The mixture was passed through a solution of ethyl magnesium bromide in tetrahydrofuran, and the unreacted component, allene, was swept by a stream of dry nitrogen while the solution was being refluxed. The tetrahydrofuran solution of propynyl magnesium bromide thus obtained was hydrolyzed by a solution of deuterium oxide (15 g.) in tetrahydrofuran, yielding 14 ml. (−78°C) of propyne-1-d_1. A trace of impurity, ethane-1-d_1, was removed by repeated distillation. The infrared spectrum of the product showed no absorptoin at 3300 cm^{-1}.

Propylene-d_6.—The Lindlar catalyst was prepared as follows. Palladium chloride was dissolved in dilute hydrochloric acid and then absorbed on pumice[10] (Pd/pumice=1/100) by evaporating the solvent. The supported palladium chloride (10 g.) was reduced in a stream of hydrogen at 300°C, and then the cooled catalyst was poisoned by treating it with an aqueous solution of 0.34 g. $Pb(OAc)_4 \cdot 3H_2O$. Propyne-1, 3, 3, 3-d_4 (12 ml. of a liquid at −78°C) was reduced in the stream of deuterium at a flow ratio of $CD_3C{\equiv}CD/D_2=1.2$ at 60～90°C over 8 g. of the Lindlar catalyst. The catalyst had been pretreated by deuterium three times at 70°C in vacuo before use. The product was 6 ml. (at −78°C) of a liquid, which was found to be composed of 15.7% deuterated propane, 78.7% propylene and 6.0% unreacted propyne. The crude product was freed from propyne by treatment with a mixed solution of mercuric iodide (0.4 g.), potassium iodide (0.5 g.), potassium hydroxide (0.3 g.) and water (3 ml.) in a pressure-glass bottle at room temperature. The final product was found to be composed of 14.7% propane-d_8 and 85.3% propylene-d_6. The degree of the deuteration of propane-d_8 was found to be 78.7% by mass spectrography. That of propylene-d_6 could not be measured directly from a mass spectrum, but it may be estimated at 82% if we assume that the same order of impurity was introduced at each step of the reduction.

Dibromoethane-d_4.—Acetylene-d_2, deuterium bromide and dibromoethane-d_4 were prepared by the method of Leitch.[15] The yield of acetylene-d_2 was 75% and that of deuterium bromide was 94% based on deuterium oxide. Dibromoethane-d_4 was obtained by photochemical addition reaction in a vacuum system. The crude product was washed with a dilute aqueous solution of potassium carbonate, dried with sodium sulfate, and distilled; b. p. 128～129°C. The yield was 93% from acetylene.

Vinyl-bromide-d_3.—In a 500 ml. three-necked flask equipped with a stirrer, a Dimroth condenser cooled at 20°C and a dropping funnel, a mixture of 120 ml. of water, 200 ml. of ethanol and 20 g. of potassium hydroxide was placed. Dibromoethane-d_4 (80 g.) was stirred into the mixture at 50°C. Vinyl-bromide-d_3 gas was evolved gradually for 2 hr. and was then condensed in a cold trap. The crude product was dried over calcium chloride overnight and then distilled through a Vigreux column, yielding 14.1 g. of the product (31%) (b.p. 17.3°C).

Propylene-1, 1, 2-d_3.—In a 200 ml. two-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser with a gas outlet tube, a dioxane solution of vinyl magnesium bromide-d_3 was prepared under nitrogen from magnesium (2.92 g.) vinyl-bromide-d_3 (12.9 g.), and tetrahydrofuran (50 ml.). The content of the flask was degassed twice and covered with nitrogen. The outlet tube was connected with a trap kept at −20°C and then with a trap cooled at −78°C. Then, 15.2 g. of dimethyl sulfate dissolved in 10 ml. of tetrahydrofuran was vigorously stirred in at room temperature over a one-hour period and heating was continued for an additional two hours. The evolved gaseous product was condensed in the second trap. The yield was 70% (6 ml. at −78°C). The product was found to contain small amounts of ethane and butadiene, which were removed by repeated distillation.

Polymerization.—Polymerizations were carried out in glass pressure tubes. The monomer was charged in vacuo into the tube in which Ziegler-Natta catalyst had previously been prepared, and it was polymerized with occasional shaking at 60°C. The polymerization was quenched by the addition of a methanol-concentrated hydrochloric acid mixture. The precipitated polymer was washed with methanol and dried in vacuo. The atactic part of the polymer was removed by extraction with boiling heptane for 10 hr.

Copolymerization.—Propylene-1, 1, 2-d_3 (0.526 g.) and propylene (0.415 g.) were charged and weighed successively. The mixture of the monomers was transferred by vacuum technique to the polymerization tube containing the catalyst and polymerized for 5.3 hr.

Artificial Mixture.—A mixture of isotactic polypropylene-1, 1, 2-d_3 and isotactic polypropylene was dissolved in toluene at 130°C and precipitated by pouring the hot solution into methanol.

15) L. C. Leitch and A. T. Morse, *Can. J. Chem.*, **30**, 924 (1952).

Summary

The synthesis of propylene-d_6 and propylene-1, 1, 2-d_3 has been attempted for the purpose of an infrared spectroscopic study of the isotactic polymers.

Propylene-d_6 has been synthesized by the half-deuteration of the propyne-d_4 which had been obtained by the hydrolysis of magnesium carbide with deuterium oxide, and propylene-1, 1, 2-d_3 has been synthesized by the reaction of deuterovinyl magnesium bromide and dimethyl sulfate. In the half-reduction of propyne-d_1 with a Lindlar catalyst, it was found that an equilibrium between propyne-1-d_1 and allene-1-d_1 exists on the catalyst.

The polymerization of these monomers was carried out with a Ziegler-Natta catalyst, and

isotactic polymers were obtained. In the copolymerization of propylene and propylene-1, 1, 2-d_3 with a Ziegler-Natta catalyst, it was observed that some of the infrared crystalline sensitive bands of isotactic polypropylene, 1164, 998 and 838 cm^{-1}, do not exist (or at least diminish) in the copolymer but do exist in artificial mixtures of the homopolymers. This fact evidently suggests that these infrared bands are due to an intrachain interaction in the crystalline part of the polymer.

Department of Polymer Science
Faculty of Science
Osaka University
Nakanoshima, Osaka (S. M. & S. N.)

Institute of Physical & Chemical Research
Bunkyo-ku, Tokyo (K. Y.)